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(54) Low pressure drop heat exchange reformer

(57) Syngas production process and reforming exchanger (100). The process involves passing a first portion of hydrocarbon feed mixed with steam and oxidant through an autothermal catalytic steam reforming zone to form a first reformed gas of reduced hydrocarbon content, passing a second portion of the hydrocarbon feed mixed with steam through an endothermic catalytic steam reforming zone (118) to form a second reformed gas of reduced hydrocarbon content, and mixing the first and second reformed gases and passing the resulting gas mixture through a heat exchange zone for cooling the gas mixture and thereby supplying heat to the endothermic catalytic steam reforming zone. The endothermic catalytic steam reforming zone and the heat exchange zone are respectively disposed tube side and shell side within a shell-and-tube reforming exchanger. The reforming exchanger comprises a plurality of tubes (118) packed with low pressure drop catalyst-bearing monolithic structures wherein an inside diameter of the tubes is less than 4 times a maximum edge dimension of the catalyst structures.

EP 1 277 698 A2

Description

Field of the Invention

[0001] This invention relates to reforming exchangers for syngas production, and more particularly to reforming exchangers with catalyst tubes having a relatively low ratio of inside tube diameter to catalyst particle size.

Background of the Invention

[0002] Steam reforming of a hydrocarbon to manufacture syngas is a very well known process. One popular technique is to use an autothermal reformer in conjunction with a reforming exchanger, as described in U.S. Patent 5,011,625 to Le Blanc, which is hereby incorporated by reference herein in its entirety. Briefly, the hydrocarbon and an oxygen source are supplied to the autothermal reformer. The combustion reaction is exothermic and supplies the heat needed for the catalytic reforming reaction that occurs in the autothermal reformer, which is endothermic, to produce a relatively hot reformed gas. The hot gas from the autothermal reformer is then used as a heat source in the reforming exchanger, which is operated as an endothermic catalytic steam reforming zone. In the reforming exchanger, a feed comprising a mixture of steam and hydrocarbon is passed through catalyst-filled tubes. The outlet ends of the tubes discharge the endothermically reformed gas near the shell side inlet where it mixes with the hot gas from the autothermal reformer. The hot gas mixture is then passed countercurrently across the tubes in indirect heat exchange to supply the heat necessary for the endothermic reforming reaction to occur.

[0003] Reforming exchangers are in use commercially and are available, for example, from Kellogg Brown & Root, Inc. under the trade designation KRES. Various improvements to the reforming exchanger design have been made, as disclosed in, for example, U.S. Patent 5,362,454 to Cizmar et al., which is hereby incorporated by reference herein in its entirety.

[0004] The present invention addresses improvements to the basic reforming exchanger design. The primary design consideration is to minimize the capital cost of the equipment, which is complicated because expensive alloys must be used to construct the tube bundle and tube sheets for the relatively high operating temperatures and pressures. Another design consideration is to maximize the capacity of the reforming exchanger within the practical limits of fabrication capabilities. It is also desirable to minimize the size and weight of the reforming exchanger to facilitate maintenance operations that require removal of the tube bundle.

[0005] Our approach to reducing the capital cost and increasing the capacity of the reforming exchanger is to increase the heat transfer rate by increasing the surface area available for heat transfer. Increasing the length of the conventional catalyst-filled tubes in the existing reforming exchanger design, however, was not practical because the tube side pressure drop (ΔP) would increase beyond that permitted without unduly complicating the tube sheet and tube sheet support designs, as well as increasing upstream operating pressures and compression costs. Furthermore, longer tubes would complicate the maintenance operations involving removal of the tube bundle.

[0006] The other approach to increasing the heat transfer area is to reduce the diameter of the catalyst-filled tubes. However, it was a commonly held belief among the reforming reactor designers that the inside diameter of the heat transfer tubes had to be a minimum of 5 times the diameter or other largest edge dimension of the catalyst particles, supposedly because of packing, bridging, flow channeling, and other potential problems. For example, James T. Richardson, Principles of Catalyst Development, Plenum Press, New York, New York, p. 8 (1986) (citing E.G. Christoffel, "Laboratory Reactors and Heterogeneous Catalytic Processes," Catal. Rev. - Sci. Eng., vol. 24, p. 159 (1982)), reports that the reactor to particle diameter ratio should be from five to ten, with the reactor length at least 50-100 times the particle diameter, to ensure that the flow is turbulent, uniform, and approximately plug flow.

[0007] To observe these design criteria would mean that reducing the tube diameter and increasing the number of tubes, as a means of increasing the available surface area, would require using a smaller catalyst structure. For example, in tubes having a 2-in. inside diameter (ID), the longitudinally bored, cylindrical catalyst shapes, also known as Raschig rings, prevalent in reforming exchangers used in the art would typically measure 0.315-in. outside diameter (OD) by 0.125-in. ID by 0.31-in. long. When small-ID tubes were specified, it was thought that the size of the catalyst particles had to be correspondingly reduced to adhere to the traditional equation $D_t/D_p > 5$, wherein D_t is the inside diameter of the tubes in the reforming exchanger and D_p is the maximum edge dimension of the catalyst structure. Unfortunately, the use of smaller catalyst particles in smaller tubes, to observe this conventional design criterion, resulted in an unacceptable increase in tube side pressure drop. Conversely, because existing reforming exchanger designs were already at or near the maximum ratio of catalyst size to tube ID, the catalyst size could not be increased in the existing tube design as a means for reducing the pressure drop per unit of tube length so as to allow the use of longer tubes. It appeared as if there would be no practical way to increase the heat transfer, and that the ultimate capacity limits of the reforming exchanger design had been reached.

Summary of the Invention

[0008] In the investigation of the present reforming exchanger designs, it was observed that the endothermic catalytic reforming reaction in the reforming exchanger is limited by heat transfer and not limited by catalyst activity. In other words, increasing the heat transfer between the shell side and tube side fluids in the reforming exchanger would tend to increase the rate of reaction, whereas increasing or decreasing the catalyst activity or surface area would have less effect on the reaction rate. With this observation, the present applicants are able to increase the heat transfer coefficients by using catalyst that has a relatively low tube side pressure drop (ΔP), but does not necessarily have an equivalent catalytic activity or geometric surface area. Further, the present applicants discovered that by carefully packing the tubes with the catalyst particles, the conventional design relationship between the catalyst diameter, D_p, and the tube inside diameter, D_t, is not applicable, and that a D_t/D_p ratio of preferably less than 4, and more preferably 3 or less, is employed to reduce the pressure drop in smaller inside diameter (ID) tubes. Quite surprisingly, the present applicants also discovered that the use of smaller ID tubes with a smaller D_t/D_p ratio results in higher heat transfer coefficients and greater efficiency than tubes designed with a conventional D_t/D_p ratio.

[0009] The present invention thus provides a solution to the dilemma in the prior art reforming exchanger designs. The present invention is the discovery of a tube design in a syngas reforming exchanger employing a catalyst structure and/or arrangement that allows the use of relatively long and/or relatively small-ID tubes. The catalyst-packed tubes can have a lower D_t/D_p ratio than in the prior art reforming exchangers. This allows the capacity of the reforming exchanger to be increased for a given size. Alternatively or additionally, the size and cost of the reforming exchanger for a given syngas production capacity can be significantly reduced.

[0010] In one aspect, the invention provides a syngas production process comprising: (1) passing a first portion of a hydrocarbon feed mixed with steam and oxidant through an autothermal catalytic steam reforming zone to form a first reformed gas of reduced hydrocarbon content; (2) passing a second portion of the hydrocarbon feed mixed with steam through an endothermic catalytic steam reforming zone to form a second reformed gas of reduced hydrocarbon content; (3) mixing the first and second reformed gases and passing the resulting gas mixture through a heat exchange zone for cooling the gas mixture and supplying heat to the endothermic catalytic steam reforming zone; (4) wherein the endothermic catalytic steam reforming zone and the heat exchange zone are respectively disposed tube side and shell side within a shell-and-tube reforming exchanger comprising a plurality of tubes packed with catalyst-bearing monolithic structures, wherein D_t/D_p is not more than 4, wherein D_t is the inside diameter of the tubes and D_p is a maximum edge dimension of the catalyst structures; and (5) recovering syngas comprising the cooled gas mixture.

[0011] In another aspect, the invention provides apparatus for reforming a hydrocarbon to produce syngas. The apparatus includes means for passing a first portion of a hydrocarbon feed mixed with steam and oxidant through an autothermal catalytic steam reforming zone to form a first reformed gas of reduced hydrocarbon content. Means are provided for passing a second portion of the hydrocarbon feed mixed with steam through an endothermic catalytic steam reforming zone to form a second reformed gas of reduced hydrocarbon content. Means are also provided for mixing the first and second reformed gases and passing the resulting gas mixture through a heat exchange zone for cooling the gas mixture and supplying heat to the endothermic catalytic steam reforming zone. The endothermic catalytic steam reforming zone and the heat exchange zone are respectively disposed tube side and shell side within a shell-and-tube reforming exchanger comprising a plurality of tubes packed with catalyst-bearing monolithic structures. The tubes have an inside diameter that is not more than 4 times a maximum edge dimension of the catalyst structures. Means are further provided for recovering syngas comprising the cooled gas mixture.

[0012] In a further aspect, the invention provides a syngas reforming exchanger. The exchanger has a tube side fluid inlet, a shell side fluid inlet and outlet, and an elongated shell having relatively high and low temperature ends. The shell side fluid inlet is adjacent to the high temperature end for receiving a hot gas feed. The tube side fluid inlet is adjacent to the low temperature end for receiving a feed mixture of hydrocarbon and steam. The shell side fluid outlet is fluidly isolated from the tube side fluid inlet by a tube sheet that is adjacent to the low temperature end for discharging cooled gas from the reforming exchanger. A tube bundle is made up of a plurality of tubes and one or more longitudinally spaced transverse baffle plates. The tubes have an inlet end secured to the tube sheet for receiving the feed mixture and an outlet end that is adjacent to the shell side fluid inlet for discharging reformed gas into the hot gas feed. Catalyst-bearing monolithic structures are disposed within the tubes for converting the gas feed mixture to reformed gas. The tubes have an inside diameter that is not more than 4 times a maximum edge dimension of the catalyst structures.

[0013] In the process, apparatus and reforming exchanger, the tubes preferably have an L_t/D_t ratio of at least 300, wherein L_t is the length of the catalyst packing in the tubes. The combination of the tube ID and the catalyst-bearing monolithic structures preferably results in a higher heat transfer rate for the same given pressure drop, i.e. wherein an overall heat transfer rate is at least 5 percent greater for a given pressure drop than Raschig rings measuring 0.31-in. long by 0.31-in. outside diameter by 0.125-in. inside diameter in tubes having an inside diameter of 2-in.

[0014] The catalyst-bearing monolithic structures, in one embodiment, comprise a twisted tape insert. The twisted tape insert is preferably made of nickel or a nickel alloy, and can have a wash-coated surface impregnated with a

nickel-containing catalyst. The twisted tape insert can have a length that is coextensive with the catalyst-packed length of the tubes and an OD that is about equal to the tube ID, such that D_t/D_p is substantially less than 1, taking the length of the twisted tape insert as the longest edge dimension for D_p as defined above.

[0015] In another embodiment, the catalyst-bearing monolithic structures comprise a central longitudinal runner and a plurality of bristles extending transversely therefrom. The bristles can be wash-coated and impregnated with a nickel-containing catalyst. Again, the runner can have a length that is coextensive with the catalyst-packed length of the tubes and an OD that is about equal to the tube ID, such that D_t/D_p is substantially less than 1, again taking the length of the runner as the longest edge dimension for D_p as defined above.

[0016] In a further embodiment, the catalyst-bearing monolithic structures comprise ceramic foam. The ceramic foam can be made by filling voids in an organic sponge substrate with a fluidized ceramic precursor and burning the substrate away to form the ceramic foam. The ceramic foam can be impregnated with nickel or another catalytically active material, and is preferably made in sheets, plugs are cut from the sheets having a diameter less than a thickness, and a plurality of the plugs are stacked end-to-end in each tube. The ceramic foam plugs preferably have a length or height that is about equal to or greater than the ID of the tubes and an OD that is about equal to the tube ID, such that D_t/D_p is approximately 1.

[0017] Still further, in another embodiment, the catalyst-bearing monolithic structures comprise finned, hollow cylinders, also called ribbed rings. The ribbed rings preferably have a longitudinal bore formed along a central axis. The depth of channels between the fins, i.e. the radial height of the fins, is preferably from 0.1 to 0.3 times the outside diameter (OD) of the structures, measuring to an outer diameter of the fins. The ribbed rings can have a length that is roughly 1/3 to 1/4 the tube ID, such that D_t/D_p is from about 3 to about 4.

Brief Description of the Drawings

[0018]

Fig. 1 is a schematic view of a reforming exchanger.

Figs. 2A and 2B are end and perspective views, respectively, of a ribbed ring catalyst support according to one embodiment of the invention.

Fig. 3 is a perspective view, partially cut away, of the ribbed ring catalyst support of Figs. 2A and 2B packed in a tube of the reforming exchanger according to the invention.

Fig. 4 is a perspective view, partially cut away, of a twisted tape catalyst monolith insert in a tube of the reforming exchanger according to another embodiment of the invention.

Fig. 5 is a perspective view, partially cut away, of a brush catalyst monolith insert in a tube of the reforming exchanger according to a further embodiment of the invention.

Figs. 6A and 6B are end and perspective views, respectively, of a plug-shaped ceramic foam catalyst support according to another embodiment of the invention.

Fig. 7 is a perspective view, partially cut away, of the ceramic foam catalyst support of Figs. 6A and 6B packed in a tube of the reforming exchanger according to the invention.

Fig. 8 is a bar chart comparing the heat transfer/pressure drop ratio for ribbed ring, Raschig ring and foam catalyst supports in 1.38-in. or 1.05-in. inside diameter (ID) tubes, and for ribbed rings in a 1.94-in. ID tube, in a reforming exchanger, relative to Raschig rings in a 1.94-in. ID tube.

Description of the Invention

[0019] Referring to Fig. 1, there is shown a reforming exchanger **100** generally built according to the disclosures in the LeBlanc and Cizmar et al. patents mentioned above, and also incorporating the principles of the present invention. The reforming exchanger **100** has a tube side fluid inlet **102**, shell side fluid inlet **104**, and shell side fluid outlet **106** in an elongated shell **108** having respective relatively high and low temperature ends **110** and **112**, respectively. The shell side fluid inlet **104** is adjacent to the high temperature end **110** for receiving a hot gas feed. The tube side fluid inlet **102** is adjacent to the low temperature end **112** for receiving a feed mixture of hydrocarbon and steam. The shell side fluid outlet **106** is fluidly isolated from the tube side fluid inlet **102** by tube sheet **114** that is adjacent to the low temperature end **112** for discharging cooled gas from the reforming exchanger **100**.

[0020] A tube bundle **116** is made up of a plurality of tubes **118** and one or more longitudinally spaced transverse baffle plates **120**. The tubes **118** have an inlet end **122** secured to the tube sheet **114** for receiving the gas mixture, and an outlet end **124** that is adjacent to the shell side fluid inlet **104** for discharging reformed gas into the hot gas feed. Low pressure drop (ΔP) catalyst-bearing monolithic structures (see Figs. 2-7) are disposed within the tubes for converting the gas feed mixture to reformed gas.

[0021] The tubes **118** preferably have a ratio of L_t/D_t of at least 300, more preferably at least 450 - 500. In determining

L_t/D_t, the diameter D_t refers to the inside diameter of the tubes **118** in the case of right circular cylindrical tubes, or to the equivalent hydraulic diameter in the case of non-circular tubes. The length L_t refers to the catalyst-filled or -packed length. Higher L_t/D_t ratios are preferred in the present invention because the heat transfer coefficients are generally higher than with a lower L_t/D_t ratio, and the resulting equipment cost is lower. A longer, smaller-ID catalyst tube **118** generally results in more tubes **118** in the tube bundle **116**, but the tube bundle **116** has a smaller diameter for a given conversion capacity, allowing the use of a shell **108** that has a smaller diameter. In general, the reduction of the diameter of the shell **108** and tube bundle **116** results in more capital cost savings than result from any increase in the length thereof, and thus the reforming exchanger **100** of the present invention can be much cheaper to fabricate than a prior art reforming exchanger of equivalent capacity. This result is particularly advantageous in the design of a new reforming exchanger **100**.

[0022] Or, if it is desired to use the same shell diameters and tube lengths of a prior art reforming exchanger so that the capital costs thereof are substantially equivalent, then the conversion capacity of the reforming exchanger **100** is substantially increased. This latter result is particularly advantageous in the retrofitting of existing reforming exchangers by replacing the existing tube bundle with a tube bundle **116** that has relatively more smaller-ID tubes **118** so that the retrofitted reforming exchanger **100** has a higher capacity than the original reforming exchanger.

[0023] In the present invention, the ratio of the tube inside diameter (ID), D_t, to the largest edge dimension of the catalyst structure (D_p) can be relatively small compared to the same ratio in conventional reforming exchangers. For example, in prior art reforming exchangers employing Raschig ring catalyst measuring 0.31-in. OD by 0.125-in. ID by 0.31-in. long, the minimum tube ID was about 2 inches. In the present invention, the same Raschig ring catalyst can be used in approximately 1.25-in. or even 1-in. ID tubes with an equivalent or slightly higher ratio of heat transfer to pressure drop. In the present invention, the D_t/D_p ratio is preferably not more than 4, and more preferably about 3 or less.

[0024] A low ΔP catalyst structure is defined herein as any suitable catalyst structure that results in a higher rate of heat transfer per unit of tube side pressure drop than in 2-in. ID reforming exchanger tubes filled with catalyst-supporting Raschig rings measuring 0.31-in. OD by 0.125-in. ID by 0.31-in. long under similar operating conditions and conversions.

[0025] Several different types of low ΔP monolithic catalyst support structures are contemplated as being useful in the present invention. While the low ΔP is the most important property in the present invention, the exemplary catalysts are also typically found to have a relatively high void fraction and present a tortuous flow path to the tube side fluid. Catalyst activity can be relatively low to moderate without significant reduction in conversion rates, although there is no general detriment to using a high activity catalyst aside from the typically higher cost involved.

[0026] With reference to Figs. 2A, 2B and 3, the catalyst support **200** is a ribbed ring catalyst structure comprising an overall cylindrical shape with a central longitudinal bore **202** and exterior ribs **204** running parallel to a longitudinal axis. The depth of the V-shaped channel **206** between the ribs is preferably from 0.1 to 0.3 times the OD of the support **200.** Supports **200** measuring 2.362-in. (6 mm) OD by 0.787-in. (2 mm) ID by 2.362-in. (6 mm) long with a fin **204** height of 0.787-in. (2 mm) comprise one example of a suitably dimensioned support **200** for use in nominal 1-inch or 1.5-inch tubes.

[0027] The ribbed ring supports **200** can be made by pressing a ceramic precursor into molds with a pin to make the central bore **202**, followed by calcining the material at elevated temperatures, e.g. 2500°F, to form a ribbed ring support made of an α-alumina, for example, and impregnating the α-alumina with nickel or another suitable catalytically active material. Ribbed ring catalyst is commercially available, for example, from Süd-Chemie Inc. of Louisville, Kentucky. Because of the relatively large size of the ribbed ring catalyst compared to the tube **118** ID, the catalyst should preferably be loaded into the tubes **118** using a dense loading method such as is accomplished with the equipment and methodology described in U.S. Patents 6,132,157, 5,897,282, and 5,890,868, which are hereby incorporated herein by reference, in order to minimize any packing or bridging problems.

[0028] With reference to Fig. 4, the catalyst insert **300** is in the form of a twisted tape having an OD about the same as the ID of the tube **118** in which it is used. The OD of the insert **300** is slightly less than the ID of the tube **118** to facilitate placement of the tape insert **300**. The length of the insert **300** can be essentially the same length as the tube with one insert **300** in each tube **118**, or multiple inserts **300** can be placed end-to-end in each tube **118**. For the multiple inserts **300**, each insert **300** preferably has a length which is at least as great as the diameter in order to keep the inserts **300** longitudinally aligned in the tube **118**. The insert **300** can be made of a catalytically active material such as nickel, or it can be coated with a catalytically active material. For example, the insert **300** can be wash coated with a ceramic as described in U.S. Patents 5,980,843 to Silversand or 5,935,889 to Murrell et al., both of which are hereby incorporated herein by reference in their entireties, and the ceramic coating impregnated with a nickel catalyst by conventional ceramic impregnation techniques. Catalytically inactive forms of such inserts **300** are commercially available for increasing the tube side heat transfer coefficients in a shell-and-tube heat exchanger from, for example, the Brown Fintube Company of Houston, Texas.

[0029] With reference to Fig. 5, the catalyst insert **400** is in the form of a brush comprising a central runner **402** and a plurality of bristles or filaments **404** extending transversely therefrom. The brush insert **400** has an OD about the

same as the ID of the tube **118** in which it is used. The length of the insert **400** can be essentially the same length as the tube **118** with one insert **400** in each tube **118**, or multiple inserts **400** can be placed end-to-end in each tube **118**, optionally with some overlap. For the multiple inserts **400**, each insert **400** should have a length which is at least several times as great as the diameter in order to keep the inserts **400** longitudinally aligned in the tube **118**. The insert **400** can be made of a catalytically active material such as nickel, or it can be coated with a catalytically active material. For example, the insert **400** can be wash coated with a ceramic as described above, and the ceramic coating impregnated with a nickel catalyst by conventional ceramic impregnation techniques. Catalytically inactive forms of such inserts **400** are commercially available for increasing the tube side heat transfer coefficients in a shell-and-tube heat exchanger under, for example, the trade designation HITRAN.

[0030] With reference to Figs. 6A, 6B and 7, the catalyst insert **500** is in the form of a ceramic foam. The ceramic foam insert **500** is preferably made by filling voids in an organic sponge substrate with a fluidized ceramic precursor and burning the substrate away to form the ceramic foam. The ceramic foam can be impregnated with nickel or another catalytically active material using conventional nickel impregnation techniques. The ceramic foam insert **500** is preferably made in sheets, plugs **502** are cut from the sheets having a diameter less than a thickness, and a plurality of the plugs **502** are stacked end-to-end in each tube **118**. If necessary, the sheet can be filled with liquid wax, which is solidified to facilitate the cutting of the plugs **502**, and then the wax is removed by melting it. The plug **502** has an OD about the same as the ID of the tube **118** in which it is used. The length of each plug **502** should be at least as great as the ID of the tube **118** to help keep the plug **502** aligned inside the tube **118**. The plugs **502** are placed end-to-end in each tube **118** as illustrated in Fig. 7.

Examples

[0031] In the following examples, the tube side heat transfer coefficients, flow rates and pressure drops are based on a tube side inlet gas having the composition in Table 1:

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[0032]

TABLE 1

Component	Mole Percent
N_2	0.23
H_2	0.34
CH_4	15.49
Ar	<0.01
CO_2	0.03
C_2H_6	1.03
C_3H_8	0.34
iC_4H_{10}	0.10
iC_5H_{12}	0.02
nC_6	0.02
CO	0.00
H_2O	82.40
Total	100.00

Examples 1-2

[0033] Conceptual sizing reviews were done on various types of catalyst sizes and tube inserts. The catalyst was of a normal size currently used in reforming exchangers available from Kellogg Brown & Root, Inc. under the trade designation KRES (Raschig rings 0.31-in. OD by 0.125-in. ID by 0.31-in. long), a smaller catalyst size (Raschig rings 0.25-in. OD by 0.10-in. ID by 0.25-in. long), a smallest catalyst size (Raschig rings 0.185-in. OD by 0.07-in. ID by

0.185-in. long), a twisted tape insert such as a Turbulator available from Brown Fintube but made of nickel 201 (99.6% nickel), and a ceramic foam insert impregnated with nickel. The results are summarized in Table 2:

TABLE 2

Parameter	Base Case	Comparative Example A	Comparative Example B	Comparative Example C	Example 1	Example 2
Catalyst	Normal (0.31 x0.125 x0.31)	Smaller (0.25 x0.10 x0.25)	Smallest (0.185 x0.07 x0.185)	Solid Pellets (0.185 x0.185)	Twisted tape	Ceramic foam
Refractory ID (in.)	103	114	110	120	48	88
Tube length (ft)	44	44	27	24	60	41
Tube OD (in.)	2	2.5	1.5	1.5	0.75	1.15
Relative no. of tubes	Base	0.79	2.03	2.33	1.61	1.62
Relative surface area	Base	0.986	0.936	0.954	0.822	0.833
Tube ΔP (psi)	28	29	28	27	10	29
Shell side ΔP (psi)	8	8	8	8	8	8
MTD (°F)	145.5	153.2	140.7	135.9	139.8	150
Overall U (Btu/hr-ft^2-°F)	55.7	53.4	63.8	65.3	68.3	60.0
Approach to equilibrium (°F)	3.6	3.4	5.1	5.9	5.1	5.3
Estimated cost (relative)	Base	1.06	0.96	0.99	0.37	0.48

[0034] These results show little or no advantage in the use of the smaller or smallest drilled cylinder catalyst shapes, or solid cylindrical pellets, Comparative Examples A, B and C, respectively. The smaller catalyst sizes result in larger diameter reactors (refractory ID), assuming that the same allowable pressure drop is available, as in Comparative Examples A, B and C. Although the tube lengths are shorter in Comparative Examples B and C, the larger reactor diameters result in premium costs and also present problems in tubesheet fabrication and quality control.

[0035] The designs with the twisted tape insert and the ceramic foam (Examples 1 and 2) use smaller diameter tubes and lattice or egg crate type baffles, resulting in longitudinal shell side flow and improved shell side performance. Combined with the enhanced tube side performance, this results in a more cost effective design with a lower pressure drop. Example 1 is based on the twisted insert measuring 0.625-in. wide by 0.035-in. thick and twisted to 4 revolutions per foot. Performance sizing assumed the same targeted methane slip (2.5%) and the same activity factors as with conventional catalysts. Nickel impregnation of a ceramic coating on the twisted tape insert can improve catalytic activity.

Example 3

[0036] Conceptual sizing reviews were done as in Examples 1-2 to compare the pressure drop and performance of Raschig ring catalyst against ribbed ring catalyst. Both catalyst structures measured 0.31-in. OD by 0.125-in. ID by 0.31-in. long, and the V-shaped grooves between the ribs on the ribbed ring catalyst were 0.17-in. deep. The results are presented in Table 3:

[Remainder of page intentionally blank]

[0037]

TABLE 3

Parameter	Comparative Example D	Example 3
Catalyst	0.31 in. x 0.125 in. x 0.31 in. Raschig rings	0.31 in. x 0.125 in. x 0.31 in. ribbed rings
Refractory ID (in.)	55	55
Tube length (ft)	25	25
Tube ID (in.)	2.00	2.00
Tube OD (in.)	2.25	2.25
Relative no. of tubes	Base	1.0
Relative catalyst volume	Base	1.0
Relative surface area	Base	1.0
Tube ΔP (psi)	21.5	12.5
Shell side ΔP (psi)	8	8
MTD (°F)	211	225
Overall U (Btu/hr- ft^2-°F)	51	48
Approach to equilibrium (°F)	33.4	29.1
Methane slip (%)	1.19	1.16

[0038] The data for Example 3 demonstrate that the performance of the ribbed ring catalyst is generally equivalent to Raschig rings of the same size, except that the tube side pressure drop is substantially lower. The cost of the ribbed ring reforming exchanger with a correspondingly reduced number of relatively longer tubes would be much less since exchanger overall length is generally less expensive than exchanger diameter.

Examples 4-5

[0039] Conceptual sizing reviews were done as in Examples 1-3 for various sizes of catalyst tube ID's (2.0, 1.55 and 1.00-in.) using standard Raschig ring catalyst. The results are presented in Table 4:

TABLE 4

Parameter	Comparative Example D	Example 4	Example 5
Catalyst	0.31 in. x 0.125 in. x 0.31 in. Raschig rings	0.31 in. x 0.125 in. x 0.31 in. Raschig rings	0.31 in. x 0.125 in. x 0.31 in. Raschig rings
Refractory ID (in.)	91.3	84.6	81.9
Tube length (ft)	40	35	25
Tube ID (in.)	2.00	1.55	1.00
Tube OD (in.)	2.25	1.75	1.125
Relative no. of tubes	Base	1.43	2.91
Relative catalyst volume	Base	0.75	0.45
Relative surface area	Base	0.964	0.912
Tube ΔP (psi)	35.5	34.5	33.8
MTD (°F)	167.9	157.9	150.2

TABLE 4 (continued)

Parameter	Comparative Example D	Example 4	Example 5
Overall U (Btu/hr-ft^2-°F)	64.7	71.4	79.9
Approach to equilibrium (°F)	6.9	8.4	14.9
Estimated cost (relative)	Base	0.84	0.64

[0040] The data for Examples 4 and 5 show, quite surprisingly, that employing smaller tubes, i.e. a lower D_t/D_p ratio, using the conventional Raschig rings, has the result of significantly reducing the catalyst volume and cost of the reforming exchanger, while maintaining the same capacity.

Example 6

[0041] Tubes of various sizes were packed with catalyst shapes comprising Raschig rings, ribbed rings and ceramic foam plugs in a laboratory tube evaluation apparatus. Air was passed through the packed tubes at Reynold's numbers similar to those seen in commercial reforming reactor tubes. The tubes were externally heated to provide tube wall temperatures within a range expected in commercial reforming reactor tubes. Heat transfer coefficients (Btu/hr-ft^2-°F) for the inside surface of the tubes were determined and pressure drop (psi/ft) was measured. The data were used to compare the ratio of heat transfer to pressure drop relative to a 1.94-in. ID tube with Raschig ring catalyst supports. The ratio was determined for Raschig rings and ribbed rings in 1.94-in. ID and 1.38-in. ID tubes, and for Raschig rings, ribbed rings and ceramic foam in 1.05-in. ID tubes. The results are presented in Fig. 8, and show that the relative ratio of heat transfer to tube side pressure drop is significantly higher for ribbed ring catalyst at all tube diameters, and for ceramic foam catalyst at the smaller tube diameter tested.

[0042] The foregoing description and examples of the invention are merely illustrative thereof. Various changes and modifications will be obvious to the skilled artisan in view of the foregoing disclosure. All such variations that fall within the scope or spirit of the appended claims are intended to be embraced thereby.

[0043] Syngas production process and reforming exchanger. The process involves passing a first portion of hydrocarbon feed mixed with steam and oxidant through an autothermal catalytic steam reforming zone to form a first reformed gas of reduced hydrocarbon content, passing a second portion of the hydrocarbon feed mixed with steam through an endothermic catalytic steam reforming zone to form a second reformed gas of reduced hydrocarbon content, and mixing the first and second reformed gases and passing the resulting gas mixture through a heat exchange zone for cooling the gas mixture and thereby supplying heat to the endothermic catalytic steam reforming zone. The endothermic catalytic steam reforming zone and the heat exchange zone are respectively disposed tube side and shell side within a shell-and-tube reforming exchanger. The reforming exchanger comprises a plurality of tubes packed with low pressure drop catalyst-bearing monolithic structures wherein an inside diameter of the tubes is less than 4 times a maximum edge dimension of the catalyst structures.

Claims

1. A syngas production process, comprising:

passing a first portion of a hydrocarbon feed mixed with steam and oxidant through an autothermal catalytic steam reforming zone to form a first reformed gas of reduced hydrocarbon content;
passing a second portion of the hydrocarbon feed mixed with steam through an endothermic catalytic steam reforming zone to form a second reformed gas of reduced hydrocarbon content;
mixing the first and second reformed gases and passing the resulting gas mixture through a heat exchange zone for cooling the gas mixture and supplying heat to the endothermic catalytic steam reforming zone;

wherein the endothermic catalytic steam reforming zone and the heat exchange zone are respectively disposed tube side and shell side within a shell-and-tube reforming exchanger comprising a plurality of tubes packed with catalyst-bearing monolithic structures, the tubes having an inside diameter that is not more than 4 times a maximum edge dimension of the catalyst structures; and
recovering syngas comprising the cooled gas mixture.

2. Apparatus for reforming a hydrocarbon to produce syngas, comprising:

means for passing a first portion of a hydrocarbon feed mixed with steam and oxidant through an autothermal catalytic steam reforming zone to form a first reformed gas of reduced hydrocarbon content;
means for passing a second portion of the hydrocarbon feed mixed with steam through an endothermic catalytic steam reforming zone to form a second reformed gas of reduced hydrocarbon content;
means for mixing the first and second reformed gases and passing the resulting gas mixture through a heat exchange zone for cooling the gas mixture and supplying heat to the endothermic catalytic steam reforming zone;

wherein the endothermic catalytic steam reforming zone and the heat exchange zone are respectively disposed tube side and shell side within a shell-and-tube reforming exchanger comprising a plurality of tubes packed with catalyst-bearing monolithic structures, the tubes having an inside diameter that is not more than 4 times a maximum edge dimension of the catalyst structures; and
means for recovering syngas comprising the cooled gas mixture.

3. A syngas reforming exchanger, comprising:

an elongated shell having relatively high and low temperature ends;
a shell side fluid inlet adjacent the high temperature end for receiving a hot gas feed;
a tube side fluid inlet adjacent the low temperature end for receiving a feed mixture of hydrocarbon and steam;
a shell side fluid outlet fluidly isolated from the tube side fluid inlet by a tube sheet adjacent the low temperature end for discharging cooled gas;
a tube bundle comprising a plurality of tubes and one or more longitudinally-spaced transverse baffle plates, wherein the tubes have an inlet end secured to the tube sheet for receiving the feed mixture and an outlet end adjacent the shell side fluid inlet for discharging reformed gas into the hot gas feed;
catalyst-bearing monolithic structures disposed within the tubes for converting the gas feed mixture to reformed gas, wherein the tubes have an inside diameter that is not more than 4 times a maximum edge dimension of the catalyst structures.

4. The invention of claim 1 wherein the tubes have an L_t/D_t ratio of at least 300 wherein L_t is taken as the length of the catalyst bearing extent of the tubes and D_t is the inside diameter of the tubes.

5. The invention of claim 2 wherein the tubes have an L_t/D_t ratio of at least 300 wherein L_t is taken as the length of the catalyst bearing extent of the tubes and D_t is the inside diameter of the tubes.

6. The invention of claim 3 wherein the tubes have an L_t/D_t ratio of at least 300 wherein L_t is taken as the length of the catalyst bearing extent of the tubes and D_t is the inside diameter of the tubes.

7. The invention of claim 4 wherein an overall heat transfer rate is at least 5 percent greater for a given pressure drop than Raschig rings measuring 0.31-in. long by 0.31-in. outside diameter by 0.125-in. inside diameter in tubes having an inside diameter of 2-in.

8. The invention of claim 5 wherein an overall heat transfer rate is at least 5 percent greater for a given pressure drop than Raschig rings measuring 0.31-in. long by 0.31-in. outside diameter by 0.125-in. inside diameter in tubes having an inside diameter of 2-in.

9. The invention of claim 6 wherein an overall heat transfer rate is at least 5 percent greater for a given pressure drop than Raschig rings measuring 0.31-in. long by 0.31-in. outside diameter by 0.125-in. inside diameter in tubes having an inside diameter of 2-in.

10. The invention of claim 1 wherein the catalyst-bearing monolithic structures comprise a twisted tape insert.

11. The invention of claim 4 wherein the catalyst-bearing monolithic structures comprise a twisted tape insert with a wash-coated surface impregnated with a nickel-containing catalyst.

12. The invention of claim 2 wherein the catalyst-bearing monolithic structures comprise a twisted tape insert.

13. The invention of claim 5 wherein the catalyst-bearing monolithic structures comprise a twisted tape insert with a wash-coated surface impregnated with a nickel-containing catalyst.

14. The invention of claim 3 wherein the catalyst-bearing monolithic structures comprise a twisted tape insert.

15. The invention of claim 6 wherein the catalyst-bearing monolithic structures comprise a twisted tape insert with a wash-coated surface impregnated with a nickel-containing catalyst.

16. The invention of claim 1 wherein the catalyst-bearing monolithic structures comprise a central longitudinal runner and a plurality of bristles extending transversely therefrom.

17. The invention of claim 4 wherein the catalyst-bearing monolithic structures comprise a central longitudinal runner, a plurality of bristles extending transversely therefrom and the bristles are wash-coated and impregnated with a nickel-containing catalyst.

18. The invention of claim 2 wherein the catalyst-bearing monolithic structures comprise a central longitudinal runner and a plurality of bristles extending transversely therefrom.

19. The invention of claim 5 wherein the catalyst-bearing monolithic structures comprise a central longitudinal runner, a plurality of bristles extending transversely therefrom and the bristles are wash-coated and impregnated with a nickel-containing catalyst.

20. The invention of claim 3 wherein the catalyst-bearing monolithic structures comprise a central longitudinal runner and a plurality of bristles extending transversely therefrom.

21. The invention of claim 6 wherein the catalyst-bearing monolithic structures comprise a central longitudinal runner, a plurality of bristles extending transversely therefrom and the bristles are wash-coated and impregnated with a nickel-containing catalyst.

22. The invention of claim 1 wherein the catalyst-bearing monolithic structures comprise ceramic foam.

23. The invention of claim 4 wherein the catalyst-bearing monolithic structures comprise ceramic foam made by filling voids in a sponge substrate with a fluidized ceramic and burning the substrate away to form the ceramic foam.

24. The invention of claim 23 wherein the ceramic foam is made in sheets, plugs are cut from the sheet having a diameter less than a thickness, and a plurality of the plugs are stacked end-to-end in each tube.

25. The invention of claim 2 wherein the catalyst-bearing monolithic structures comprise ceramic foam.

26. The invention of claim 5 wherein the catalyst-bearing monolithic structures comprise ceramic foam made by filling voids in a sponge substrate with a fluidized ceramic and burning the substrate away to form the ceramic foam.

27. The invention of claim 26 wherein the ceramic foam is made in sheets, plugs are cut from the sheet having a diameter less than a thickness, and a plurality of the plugs are stacked end-to-end in each tube.

28. The invention of claim 3 wherein the catalyst-bearing monolithic structures comprise ceramic foam.

29. The invention of claim 6 wherein the catalyst-bearing monolithic structures comprise ceramic foam made by filling voids in a sponge substrate with a fluidized ceramic and burning the substrate away to form the ceramic foam.

30. The invention of claim 29 wherein the ceramic foam is made in sheets, plugs are cut from the sheet having a diameter less than a thickness, and a plurality of the plugs are stacked end-to-end in each tube.

31. The invention of claim 1 wherein the catalyst-bearing monolithic structures comprise Raschig rings.

32. The invention of claim 2 wherein the catalyst-bearing monolithic structures comprise Raschig rings.

33. The invention of claim 3 wherein the catalyst-bearing monolithic structures comprise Raschig rings.

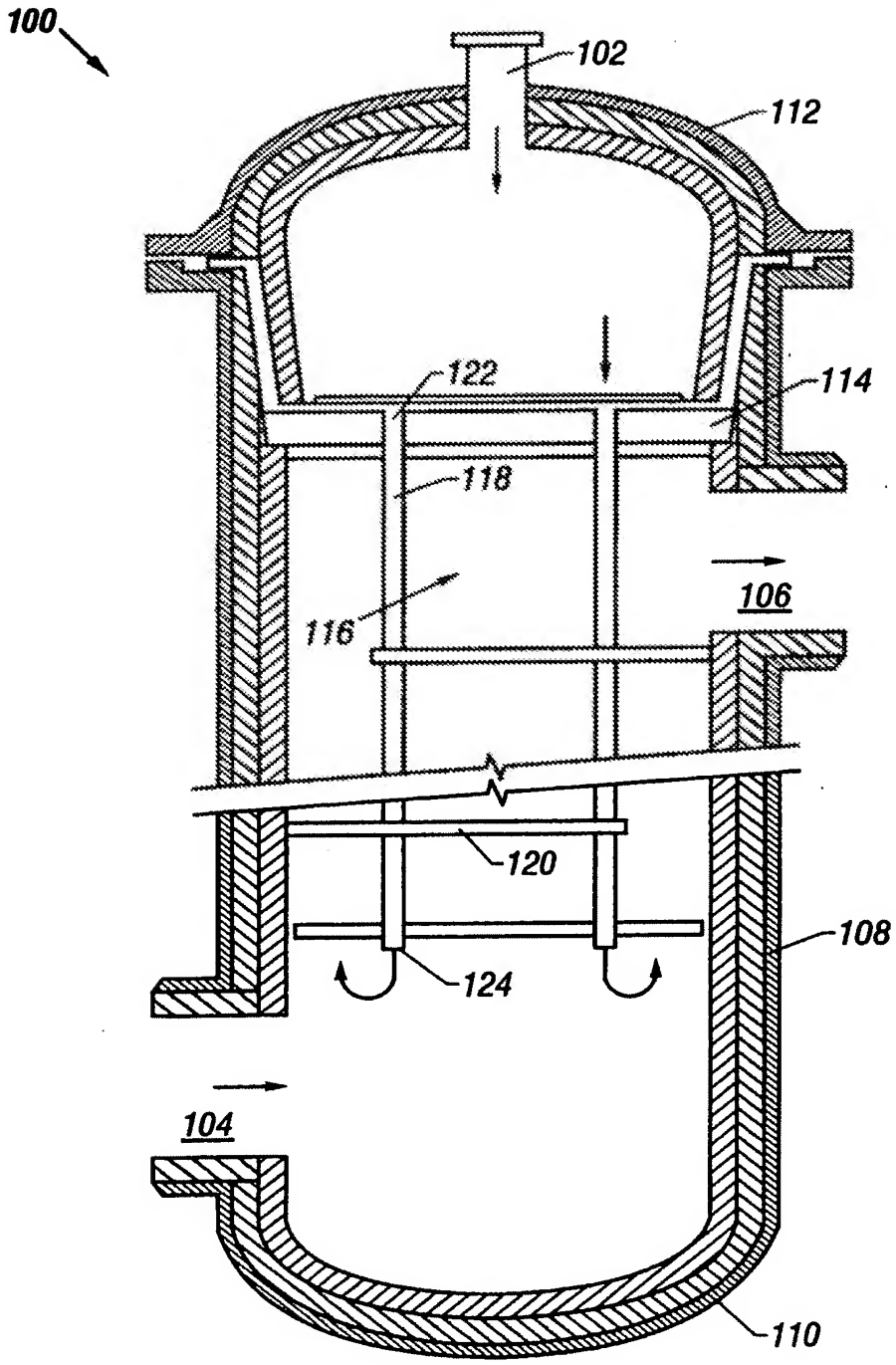

FIG. 1

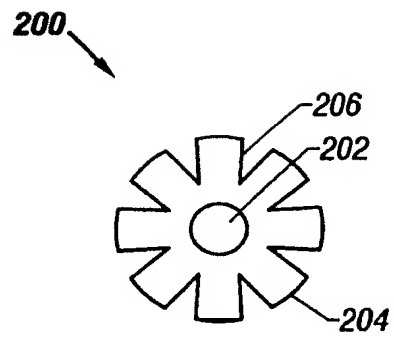

FIG. 2A

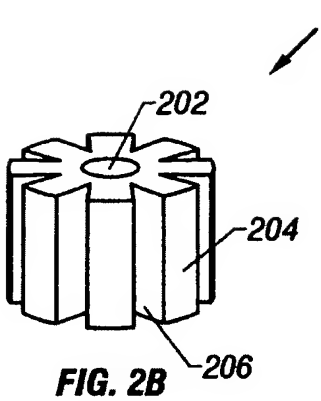

FIG. 2B

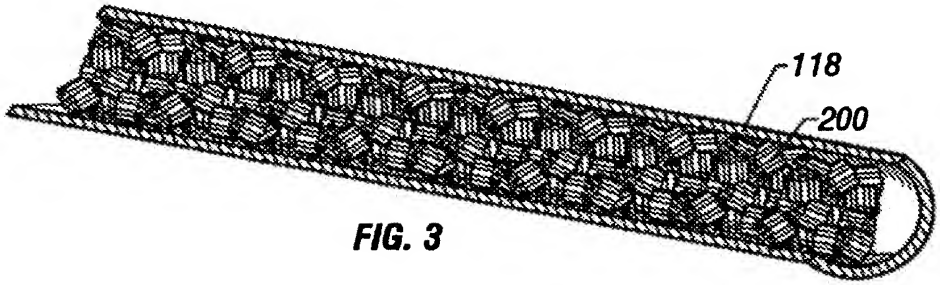

FIG. 3

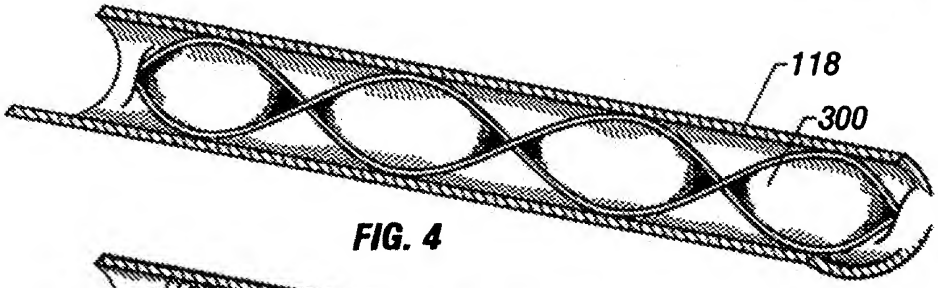

FIG. 4

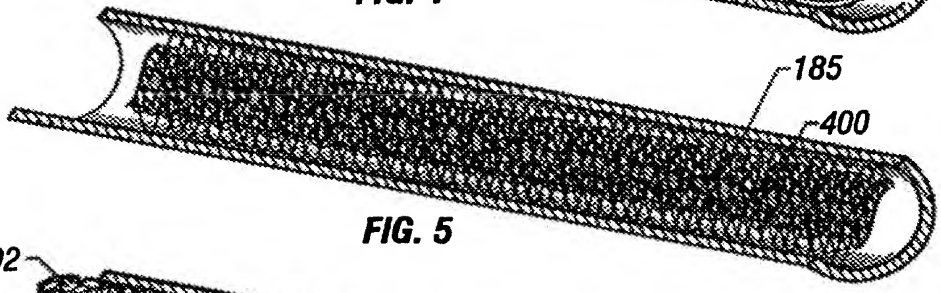

FIG. 5

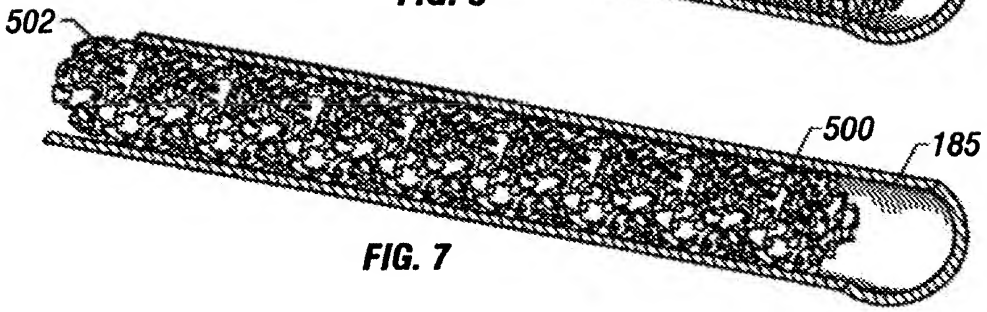

FIG. 7

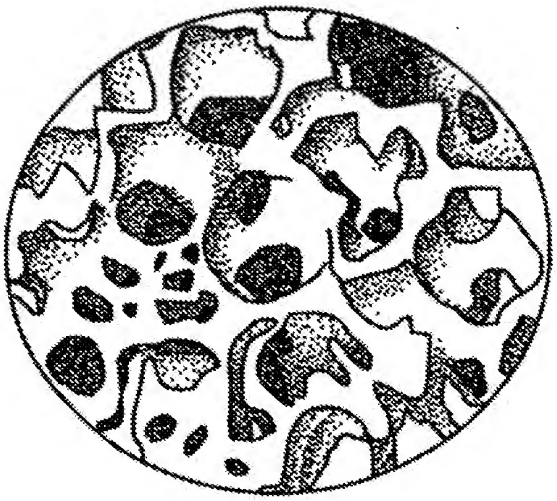

FIG. 6A

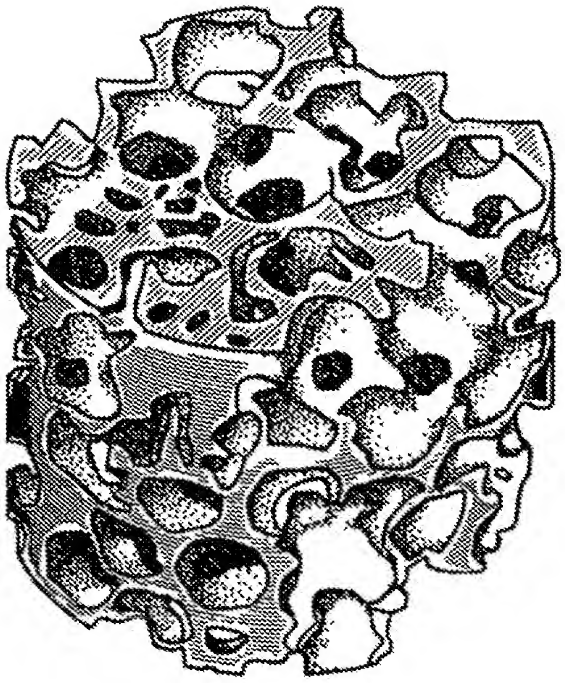

FIG. 6B

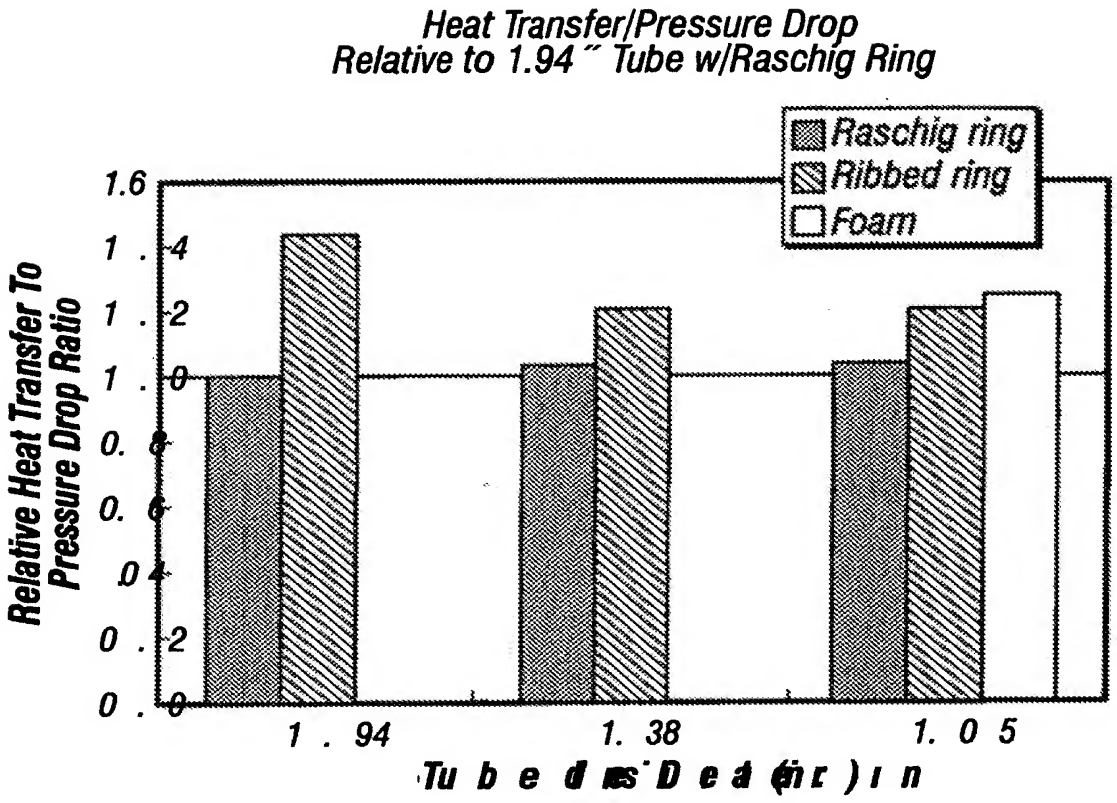
Heat Transfer/Pressure Drop
Relative to 1.94˝ Tube w/Raschig Ring
Raschig ring
Ribbed ring
Foam
Relative Heat Transfer To
Pressure Drop Ratio
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1.94
1.38
1.05
Tube Nominal Diameter (in.)

FIG. 8